GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 26, GB3018, doi:10.1029/2012GB004353, 2012

Recycling versus export of bioavailable dissolved organic matter in the coastal ocean and efficiency of the continental shelf pump

Christian Lønborg[1,2] and Xosé Antón Álvarez-Salgado[2]

Received 16 March 2012; revised 27 June 2012; accepted 8 July 2012; published 23 August 2012.

[1] At least 15% of the 2 Pg y^{-1} of dissolved organic carbon (DOC) that accumulates in the surface layer of the open ocean has been exported from the ocean margins. The C: N: P stoichiometry of the production and microbial degradation of dissolved organic matter (DOM) in the coastal ocean conditions the quality of the exported substrates. In this work, DOC, dissolved organic nitrogen (DON) and phosphorus (DOP) bioavailability measurements from published bottle incubation experiments have been compiled and reanalyzed to examine the role of bioavailable DOM (BDOM) in the coastal ocean. DOM bioavailability decreased significantly ($p < 0.001$) in the sequence DOP > DON > DOC, with bioavailable DOC (BDOC) representing 22 ± 12% (mean ± SD) of the total DOC, bioavailable DON (BDON) 35 ± 13% of the total DON and bioavailable DOP (BDOP) 70 ± 18% of the total DOP. This suggests that the role of DOM on the recycled and export production of the coastal ocean is more relevant for the P than for the N and for the N than for the C biogeochemical cycles. First-order microbial degradation rate constants (κ) of BDOM (normalized to 15°C) increased significantly ($p < 0.05$) in the same sequence, with κ_C being 0.066 ± 0.065 day^{-1}, κ_N 0.111 ± 0.096 and κ_P 0.154 ± 0.137 day^{-1}. Significant ($p < 0.001$) power relationships were found among κ_C, κ_N and κ_P (R^2 = 0.84–0.87). The C: N: P molar ratio of the DOM that resists microbial degradation was extremely depleted in N and P, 2835 (±3383): 159 (±187): 1, compared with the BDOM fraction, 197 (±111): 25 (±16): 1. The flushing time (τ) of the coastal ocean in relation to the turnover time of BDOM ($1/\kappa$), i.e., $\tau \cdot \kappa$, dictates the fate —degradation versus accumulation— of the large scale export of BDOM, which could fuel parts of the oceanic new production and influence the N/P limitation of the open ocean.

Citation: Lønborg, C., and X. A. Álvarez-Salgado (2012), Recycling versus export of bioavailable dissolved organic matter in the coastal ocean and efficiency of the continental shelf pump, *Global Biogeochem. Cycles*, *26*, GB3018, doi:10.1029/2012GB004353.

1. Introduction

[2] The key role of dissolved organic matter (DOM) in the marine food web was already suggested in the early 20th century [e.g., *Waksman and Carey*, 1935], but this view was not broadly acknowledge by the scientific community until the 1970's [e.g., *Pomeroy*, 1974; *Williams*, 1981]. DOM in marine systems has many potential sources such as fish [*Dundas*, 1985], macrophytes [*Søndergaard*, 1981; *Wada et al.*, 2008], particle hydrolysis [*Smith et al.*, 1992], plankton [*Lønborg et al.*, 2009b; *Kawasaki and Benner*, 2006], rain water [*Cornell et al.*, 1995], riverine sources [*Sobczak et al.*, 2005], and sediments [*Burdige et al.*, 2004], with the most important sources in coastal waters being riverine (terrestrial) and plankton (marine) sources [*Cauwet*, 2002].

[3] In coastal waters three processes of importance have been identified to remove DOM from the water column in: 1) biological uptake and utilization [e.g., *Lønborg et al.*, 2009a]; 2) photochemical reactions, where DOM is either transformed into refractory compounds [e.g., *Kieber et al.*, 1997], degraded directly to CO or CO2, or to compounds more bioavailable for bacterial uptake [e.g., *Moran and Zepp*, 1997]; and 3) loss via assembly into polymer gels [*Chin et al.*, 1998], aggregation or sorption to particles due to changes in ionic strength when freshwater mixes with sea water [e.g., *Sholkovitz*, 1976; *Carlson et al.*, 1985].

[4] The average radiocarbon age of DOM ranges from 90 to 6600 years [*Williams and Druffel*, 1987; *Bauer et al.*, 1992; *Beaupré and Druffel*, 2009] and, given that the residence time of the intermediate and deep ocean waters is from 80 and 2000 years [*Laurelle et al.*, 2009], part of the DOM is able to resist several ocean cycles of exposition to sunlight and bacterial degradation [*Hansell et al.*, 2012]. But a minor

[1]Centre for Sustainable Aquatic Research, College of Biosciences, Swansea University, Swansea, UK.
[2]Instituto de Investigaciónes Mariñas, CSIC, Vigo, Spain.

Corresponding author: C. Lønborg, Centre for Sustainable Aquatic Research, College of Biosciences, Swansea University, Wallace Building, Swansea SA2 8PP, UK. (clonborg@gmail.com)

variable part of carbon, nitrogen and phosphorus bound in the DOM pool can be consumed by microbes over short periods (days to weeks), which varies over seasons [*Carlson et al.*, 1994; *Williams*, 1995], diurnal periods [*Coffin et al.*, 1993; *Zweifel et al.*, 1993] and between studies. DOM bioavailability (BDOM) is a function of the chemical composition, the enzymatic capability of the organisms involved, and the physical and chemical conditions of the environment. The term "bioavailable" or "labile" DOM does not have any strict time constrain as there is no way of linking bioavailability to any particular chemical characteristic of BDOM. Therefore, it remains an operationally defined term whose quantification depends on the method selected, experimental conditions (e.g. temperature and nutrients) and the time scale used.

[5] From an operational point of view, it is important to distinguish between the BDOM that is processed within the ecosystem studied and the BDOM that escapes utilization. The first fraction, which we term "labile DOM", contributes to the regenerated production (RP) of the ecosystem because N and P are returned to the same plankton population that ultimately produced the BDON and BDOP. The second fraction, which we term "semilabile DOM", contributes to the export or new production (NP) of the ecosystem, because it feeds an ecosystem adjacent to the one in which it was produced. On average, 20–40% of the ocean total production (TP = NP + RP) is thought to be recycled through DOM [*Carlson*, 2002]. The remaining DOM, which we term "resistant DOM" (RDOM), comprises the long term variability, and are transported over long distances by the large scale ocean circulation. The relative importance of both BDOM fractions will depend upon the BDOM degradation rate constants (κ) in relation to the flushing time of the study ecosystem (τ). If $\kappa < 1/\tau$, most of the BDOM will be labile, whereas if $\kappa > 1/\tau$ it will be semi-labile [*Lønborg et al.*, 2010]. BDOM can accumulate in marine systems because of bacterial nutrient limitation [*Rivkin and Anderson*, 1997], protist grazing [*Thingstad et al.*, 1999], temperature limitations of extra-cellular enzymes and changing permeability of the bacterial cell membrane [*Chen and Wangersky*, 1996; *Nedwell*, 1999] and production of more semi-labile DOM [*Søndergaard et al.*, 2000], favoring export compared with in situ degradation of these substrates [*Zweifel et al.*, 1995]. Some studies have pointed to that high molecular weight DOM (HMW-DOM; >1 kDa) is more reactive than low molecular weight DOM (LMW-DOM; <1 kDa) DOM, which is known as the "size-reactivity continuum theory" pointing to that changes in BDOM could be explained by varying proportion of more labile HMW-DOM compared with the slower degrading LMW-DOM [*Amon and Benner*, 1996]. The uptake of bioavailable HMW-DOM is dependent on the microbial production of ectoenzymes and extracellular enzymes [*Chróst and Rai*, 1993]. This enzymatic depolymerization and transformation may be influenced by differences in the complex structure of DOM, with variations in secondary and/or tertiary structures changing the enzymatic access to hydrolytic sites [*Del Giorgio and Davies*, 2003]. The bacterial capability of producing enzymes depends ultimately on their gene pool, suggesting that bacterial community composition and genetic diversity could partly determine BDOM degradation rates [*Mou et al.*, 2007]. However, some studies have shown that marine microbial communities are populated by taxa capable of degrading a variety of organic carbon compounds, pointing to some plasticity in the enzyme production [*Martinez et al.*, 1996; *Mou et al.*, 2008].

[6] The coastal ocean is among the most productive and biogeochemically active zones of the biosphere [*Gattuso et al.*, 1998]. It is responsible for 18–33% of the primary production, 27–50% of the export production [*Walsh*, 1991; *Wollast*, 1998; *Chen*, 2003], 83% of the benthic mineralization, and 87% of the organic matter burial of the global ocean [*Middelburg et al.*, 1993; *Dunne et al.*, 2007]. Considering that the coastal ocean represents less than 1% of the volume of the global ocean, biogeochemical processes are enhanced by about 2 orders of magnitude in the former compared with the latter. DOM is a key component of carbon and nutrient cycles in the coastal ocean: at least 0.28 Pg C, about 35% of the new production of the coastal zone, is exported to the adjacent ocean as DOM [*Chen*, 2003], which represents about 15% of the 2 Pg of DOC that accumulates each year in the surface layer of the open ocean [*Hansell et al.*, 2009].

[7] Various approaches have been used to quantify the microbial bioavailability of DOM, which can broadly be divided into microbial (*in vitro*) and geochemical (*in situ*) approaches. What we here term the "microbial incubation approach" uses a dilution of a natural microbial community to follow the utilization of DOM and/or oxygen over time in controlled laboratory conditions [*Ogura*, 1972, 1975; *Coffin et al.*, 1993]. Other microbial approach consists of using bioreactors where a natural bacterial community is allowed to colonize an inert material placed inside a column to establish a microbial biofilm. The decrease in DOM concentration after re-cycling the water sample through the column is here used as a measure of BDOM [*Badr et al.*, 2008]. Many studies also follow other microbial measurements such as bacterial growth, production, respiration, uptake of specific and stable isotope compounds as proxies for DOM utilization [*Bronk and Glibert*, 1993; *Kirchman*, 2000; *Veuger et al.*, 2004].

[8] The geochemical "mass balance approach" calculates the inputs to and outputs from a coastal system to estimate the flushing time (τ) and net excess of DOM (ΔDOM). The net ecosystem production rate of BDOM is then obtained multiplying ΔDOM by τ [e.g., *Smith and Hollibaugh*, 1997]. In the open ocean, it is common to assume that surface water DOM consist of bioavailable and resistant DOM, while in deep waters only refractory DOM is present. Therefore, the difference between the deep and surface water DOM concentrations provides an estimate of the concentration of labile plus semi-labile DOM [*Carlson*, 2002].

[9] The focus of this work is to quantify, compare, and generalize BDOM estimates obtained from microbial incubation experiments in the coastal ocean to produce a global assessment of the size and reactivity of the BDOC, BDON and BDOP pools, representing a step further compared to previous reviews by *Søndergaard and Middelboe* [1995] and *Del Giorgio and Davies* [2003]. Furthermore, our results can be used in conceptual, parametric and numerical

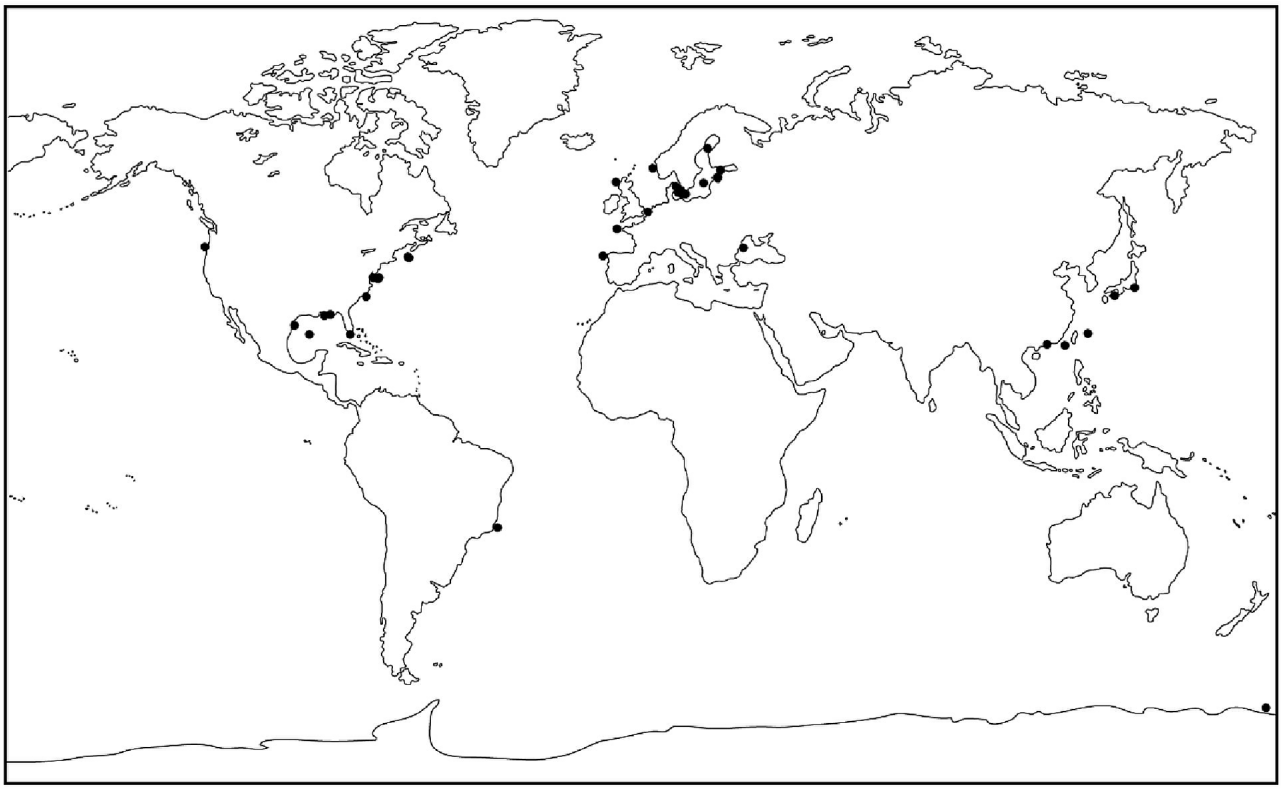

Figure 1. World map showing the location of the study sites where microbial incubations experiments were conducted to determine the degradation of dissolved organic carbon, nitrogen and/or phosphorus in the coastal ocean.

biogeochemical models of the interaction between the coastal and surface open ocean.

2. Methods

2.1. Data Collection

[10] In this study we have surveyed the literature for published estimates of DOM bioavailability in the coastal ocean. In the context of this work, BDOM is operationally defined as the organic matter consumed by heterotrophic prokaryotes within a given period of time [*Del Giorgio and Davies*, 2003] and the coastal ocean as the portion of the global ocean covering the continental margin [*Gattuso et al.*, 1998]. Open continental shelves, bays, estuaries and coastal lagoons were included in our survey, covering a wide range of latitudes and contrasting continental influences (Figure 1). In coastal systems strongly influenced by continental runoff, only samples downstream from the freshwater-seawater interface (salinity >3) were considered. The survey was restricted to data obtained from microbial incubation experiments conducted in the dark at controlled temperature, which followed the decrease in natural DOM concentration over time. Generally, an inoculum of natural water filtered through 1–2 μm pore-sized filters was added to the same water filtered through 0.1–0.2 μm pore-sized filters in a proportion of 1:10. The incubation time varied considerably between studies, from a few days to several months (see Table S1 in the auxiliary material)[1], which resulted in some studies including only the labile DOM pool while others included both the labile and semi-labile pools. The sampling interval through the incubation time was also very variable, from less than 1 day at the beginning of the incubation period to several months at the end. In addition, in some studies water for DOM analysis was not filtered and, in others, filters of different materials and pore sizes, ranging from 0.2 to 1 μm were used, with GF/F filters (nominal pore size 0.7 μm) being the most common. Therefore, in most cases part of the bacterial C, N, and P would contribute to the DOM pool. Our database consists of 1345 data points for DOC, 464 for DON and 311 for DOP (Table S1) aggregated in 328 incubation experiments for DOC, 83 for DON and 80 for DOP (Table S2). Restricting the survey to incubations experiments that lasted for >40 days, there are 175 incubation experiments for DOC, 75 for DON and 46 for DOP. Some data points presented in Table S1 were extracted from digitalized scatter plots using the software DataThief (K. Huyser and J. van der Laan, 1992, version 1.0.8).

[11] The cases are not distributed homogeneously neither geographically (Figure 1) nor temporally. One-third of the experiments corresponded to studies conducted in the Baltic sea, followed by the East coast of North America, from the Middle Atlantic Bight to the Louisiana continental shelf. Few works have dealt with the bioavailability of DOM in the Japanese and Chinese coasts, including the pioneering work

[1]Auxiliary materials are available in the HTML. doi:10.1029/2012GB004353.

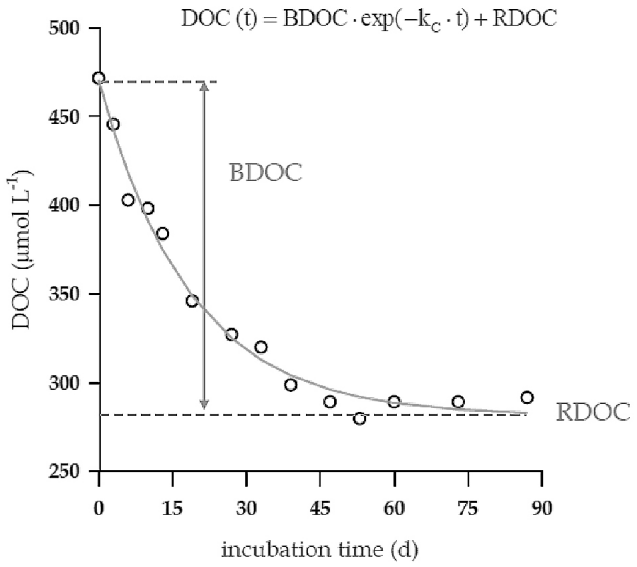

Figure 2. Time course of DOC concentration during a microbial incubation experiment conducted by *Pempkowiak* [1985] with Gdansk deep water (Baltic sea) in May 1983. The exponential decay equation was fitted using the Marquardt-Levenberg algorithm implemented in the software package Statistica 6.0. The BDOM and RDOM fractions and the exponential decay equation are shown.

of *Ogura* [1975] in Tokyo and Sagami bays. Despite of the global importance of coastal upwelling systems in terms of productivity and efficiency of DOM export to the adjacent ocean [*Hill and Wheeler*, 2002; *Álvarez-Salgado et al.*, 2007], only a few cases are available for the NW Iberian and Oregon coasts. It is remarkable the lack of data from the Central and South American, African and Australian coasts. Seasonal cycles of DOM bioavailability have been obtained only in the Bothnian sea, Darss sill, Florida bay, Georges bank, Hiroshima bay, Horsens fjord, Loch Crean, Ria de Vigo, Sacramento-San Joaquin river delta, Tokyo bay and the York river estuary (Table S2).

2.2. DOM Pools and Degradation Rate Constants

[12] The utilization of a single rate-limiting dissolved organic substrate (S) by a pure culture of microorganisms at a constant temperature can be modeled with the differential *Monod* [1949]'s equation:

$$\frac{dS}{dt} = -\frac{V_{max}}{K_S + S} \cdot S \quad (1)$$

Where S is the concentration of substrate, V_{max} the maximum utilization rate and K_S the half saturation constant. When K_S is ≥10 times S, then $V_{max}/(K_S + S) \sim V_{max}/K_S$ and equation (1) transforms into the simpler differential equation [*Bekins et al.*, 1998]:

$$\frac{dS}{dt} = -\kappa_S \cdot S \quad (2)$$

Where $\kappa_S = V_{max}/K_S$ is the first-order degradation rate constant.

[13] A batch incubation of a natural water sample is composed of myriads of different reactive dissolved organic substrates and diverse heterotrophic prokaryote communities that tend to utilize the most reactive substrates first [*Middelburg et al.*, 1993]. Consequently, κ_S, as calculated with equation (3), should decrease during the incubation time.

$$\kappa_S = \frac{\mathrm{Ln}\left(\frac{S(t_1)}{S(t_2)}\right)}{t_2 - t_1} \quad (3)$$

This model implies a continuum of reactive groups [*Middelburg et al.*, 1993]. Alternatively, a discrete number of reactive groups can be considered. In this sense, the time course of the concentration of BDOM in the bioassays reviewed in this study can be reasonably modeled by assuming that BDOM decomposes at an overall rate directly proportional to its own concentration (Figure 2). This assumption implies that two DOM pools should be considered: resistant (RDOM) and bioavailable (BDOM). RDOM is the concentration of DOM at the end of the incubation time, and BDOM the difference between the initial DOM concentration and RDOM. The decay of DOM during the course of the incubations was modeled by equation (4), which results from the integration of equation (2) with S being BDOM:

$$\mathrm{DOM}(t) = \mathrm{BDOM} \cdot \exp(-\kappa_M \cdot t) + \mathrm{RDOM} \quad (4)$$

Where DOM(t) is the concentration of DOM at time t (in μmol L^{-1}), κ_M is the degradation rate constant (in day^{-1}), and t is the time (in day). Since BDOM and RDOM were calculated prior to adjusting the time evolution of DOM(t), the only parameter that was adjusted with equation (4) was κ_M, using the Marquardt-Levenberg algorithm implemented in the software package Statistica 6.0. The two-pool model was applied only to the incubation experiments which lasted for >40 days to ensure that the remaining DOM at the end of the incubation time is resistant to microbial degradation.

[14] Batch incubations reviewed in this work were conducted both at in situ and lab controlled conditions, but covering a wide range of incubation temperatures, from 0 to 30°C (Table S1). Therefore, κ_M values obtained with equation (3) were normalized to a standard temperature of 15°C by applying equation (5), derived from the Arrhenius' equation:

$$\kappa_M(15°C) = \kappa_M(T) \cdot (Q_{10})^{\frac{10}{15-T}} \quad (5)$$

Where κ_M(15°C) and κ_M(T) are the degradation rate constants at 15°C and temperature T, respectively; and Q_{10} is the Arrhenius temperature coefficient. Q_{10} values for the microbial degradation of marine DOC have been reported by several authors [*Seiki et al.*, 1991; *Chen and Wangersky*, 1996; *Raymond and Bauer*, 2000; *Del Giorgio and Davies*, 2003; *Lønborg et al.*, 2009a] and a consensus value of 2.2 will be used in this study. However, there is a lack of studies of the temperature dependence of the microbial degradation of marine DON and DOP. To the best of our knowledge, they were only determined by *Lønborg et al.* [2009a] in a study of Loch Crean (Scotland), covering temperatures from 8°C to 18°C. Revisiting the data of that work, we obtained

Table 1. The α, β, and γ Fitting Parameters (Value $\pm$ S.E.) of the Power Functions Between the Degradation Rate Constants (κ_C, κ_N, and κ_P) and the Initial DOM Concentrations (DOC_0, DON_0, DOP_0), Refractory DOM (RDOC, RDON, and RDOP) and the Initial DOM Concentrations, and the Relations Between the Degradation Rate Constants for DOC (κ_C), DON (κ_N), and DOP (κ_P)[a]

	α ($\pm$SE)	β ($\pm$SE)	γ ($\pm$SE)	n	R^2
$\kappa_C(t) = \alpha \cdot (DOC_0/s)^{\beta} \cdot t^{\gamma}$	0.049 $\pm$ 0.002	-0.33 ± 0.03	-0.54 ± 0.02	853	0.44
$\kappa_N(t) = \alpha \cdot (DON_0/s)^{\beta} \cdot t^{\gamma}$	0.025 $\pm$ 0.003	-0.72 ± 0.08	-0.60 ± 0.05	315	0.57
$\kappa_P(t) = \alpha \cdot (DOP_0/s)^{\beta} \cdot t^{\gamma}$	0.04 $\pm$ 0.02	-0.18 ± 0.08	-0.38 ± 0.05	180	0.31
$RDOC = \alpha \cdot s^{\beta} \cdot DOC_0^{\gamma}$	1.3 $\pm$ 0.4	-0.10 ± 0.03	0.96 $\pm$ 0.04	150	0.93
$RDON = \alpha \cdot s^{\beta} \cdot DON_0^{\gamma}$	1.3 $\pm$ 0.3	-0.21 ± 0.04	0.98 $\pm$ 0.05	72	0.91
$RDOP = \alpha \cdot s^{\beta} \cdot DOP_0^{\gamma}$	0.5 $\pm$ 0.2	NS	1.3 $\pm$ 0.3	46	0.31
$\kappa_C = \alpha + \beta \cdot (\kappa_N)^{\gamma}$	0.04 $\pm$ 0.01	1.3 $\pm$ 0.2	1.7 $\pm$ 0.2	67	0.87
$\kappa_C = \alpha + \beta \cdot (\kappa_P)^{\gamma}$	0.04 $\pm$ 0.01	0.7 $\pm$ 0.1	1.5 $\pm$ 0.2	42	0.84
$\kappa_C = \alpha + \beta \cdot (\kappa_P)^{\gamma}$	0.04 $\pm$ 0.01	0.8 $\pm$ 0.1	1.2 $\pm$ 0.2	42	0.84

[a]Here n: number of data; R^2: coefficient of determination. Data were fitted to the power functions by mean of the Marquardt-Levenberg algorithm implemented in the software package Statistica 6.0. NS: Not significant.

the Q_{10} values of 2.0 for DON and 1.5 for DOP that will be used in this study.

[15] In 229 of the 491 incubation experiments summarized in Table S2 only the initial and final DOM concentrations were reported; therefore, just BDOM and RDOM can de estimated. But in the remaining 262 cases, we were able to determined κ_M from the time course of DOM concentration during the incubation time. These cases corresponded to four Baltic embayments (Horsens fjord, Darss sill, Arkona and Gdansk deep), a Norwegian fjord (Raunefjord fjord), a Scottish loch (Loch Crean), two coastal upwelling system (Oregon and NW Spain coasts), three temperate bays (Tokyo, Sagami and Long bay) and two estuaries (York river and Elorn river), two subpolar shelves (Georges bank and Hokkaido island), two subtropical coastal areas (Florida bay and the South China Sea), a coral reef (Ishigaki Island) and the Antarctic Ross sea shelf.

3. Results

3.1. Continuum Reaction Model Approach

[16] Initial concentrations of DOC varied from 50–60 μmol L^{-1}, characteristic of coastal polar, subpolar and upwelling environments relatively unaffected by continental runoff, to >1000 μmol L^{-1}, found in subtropical coastal areas strongly affected by humic-rich continental waters such as the coastal lagoons of Rio de Janeiro, the Florida bay coast in contact with the Everglades or the Sacramento-San Joaquín river delta (Tables S1 and S2). Initial concentrations of DON and DOP ranged from 4.5 to 45 μmol L^{-1} and from 0.08 to 0.50 μmol L^{-1}, respectively.

[17] In continuum reaction models, the time-dependent first-order decay parameter, $\kappa_S(t)$, follows a power functional decrease with time [*Middelburg et al.*, 1993]. In the particular case of the microbial utilization of DOM in the coastal ocean, a slightly more complex function has been needed to successfully model together all the study cases:

$$\kappa_S(t) = \alpha \cdot \left(\frac{S_0}{s}\right)^{\beta} \cdot t^{\gamma} \quad (6)$$

Where α, β and γ are fitting parameters, S_0 is the initial concentration of DOC, DON or DOP and s the salinity of the incubated coastal water. Note that the S_0/s ratio allows discriminating between high initial substrate concentrations of terrestrial or marine origin. The values of S_0/s ranged from 2 to 1342, with a mean $\pm$ SD value of 47 $\pm$ 127 (n = 300) for the case of DOC; from 0.1 to 5.7, 1.0 $\pm$ 1.2 (n = 80) for the case of DON; and from 0.002 to 0.068, 0.014 $\pm$ 0.013 (n = 67) for the case of DOP. Table 1 summarizes the fitting parameters obtained with equation (6) for DOC, DON and DOP. β is negative and its absolute value is significantly lower than 1 for the three cases, indicating that the organic carbon, nitrogen and phosphorus substrates of marine origin are more labile than those of terrestrial origin. Considering the mean value of S_0/s, $\kappa_S(0)$ of 0.014 $\pm$ 0.002, 0.025 $\pm$ 0.003 and 0.095 $\pm$ 0.005 day^{-1} can be obtained for DOC, DON and DOP. Therefore, on average, DOP is significantly ($p < 0.001$) more labile than DON, and DON significantly ($p < 0.001$) more labile than DOC. As expected, γ is also negative and its absolute value is significantly lower than 1 for DOC, DON and DOP. This parameter does not differ significantly among DOC and DON but it is significantly lower for DOP ($p < 0.05$), suggesting that DOP keeps more labile than DOC and DON through the course of the incubations.

[18] This lability gradient translates into a more efficient utilization of P over N and of N over C (Figure 3). Most of the data points on Figure 3a are above the 1:1 line, indicating that the percentage of the initial DON is larger than the percentage of the initial DOC utilized by the microbes of the coastal ocean at any incubation time. In fact, the slope of the linear regression, 1.3 $\pm$ 0.1, suggest that, on average, the BDON(t)/DON ratio is 30 $\pm$ 10% larger than the BDOC(t)/DOC ratio. The same trend is observed in Figures 3b and 3c, and the corresponding slopes, 2.4 $\pm$ 0.2 and 1.7 $\pm$ 0.1, suggest that the BDOP(t)/DOP ratio is 140% $\pm$ 20% larger than the BDOC(t)/DOC ratio and 70 $\pm$ 10% larger than the BDON(t)/DON ratio. Whereas the larger amount of BDOC(t) rarely exceeds 40% of the initial DOC, it is close to 60% in the case of DON and to 100% in the case of DOP.

[19] The initial DOM pool had a C: N: P (mean $\pm$ SD) molar ratios of 1164 $\pm$ 150: 123 $\pm$ 15: 1, while the average C: N: P stoichiometry of the utilization of DOM in the coastal ocean obtained from the slopes of the correlations of the utilized DOC versus the utilized DON (Figure 4b) and the utilized DOC versus the utilized DOP (Figure 4c) was 216 ($\pm$32): 24 ($\pm$4): 1.

3.2. Multi-G Model Approach

[20] As stated in the methods section, the two-pool model has been applied only to the incubation experiments that last

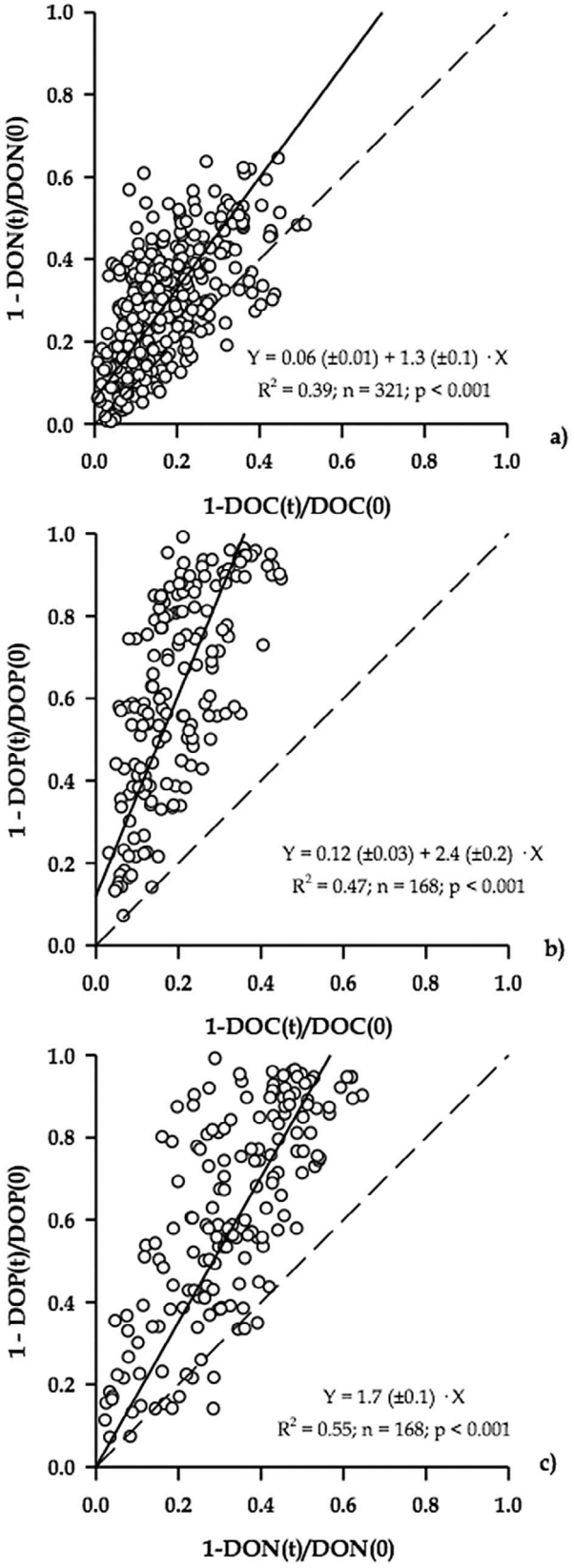

Figure 3. X-Y plots of the relationship between proportions of the initial concentrations of (a) DOC and DON, (b) DOC and DOP, and (c) DON and DOP used at all incubation time in all experiments. Dashed line, 1:1 line; solid line, linear fitting equation according to *Sokal and Rohlf* [1995] model II.

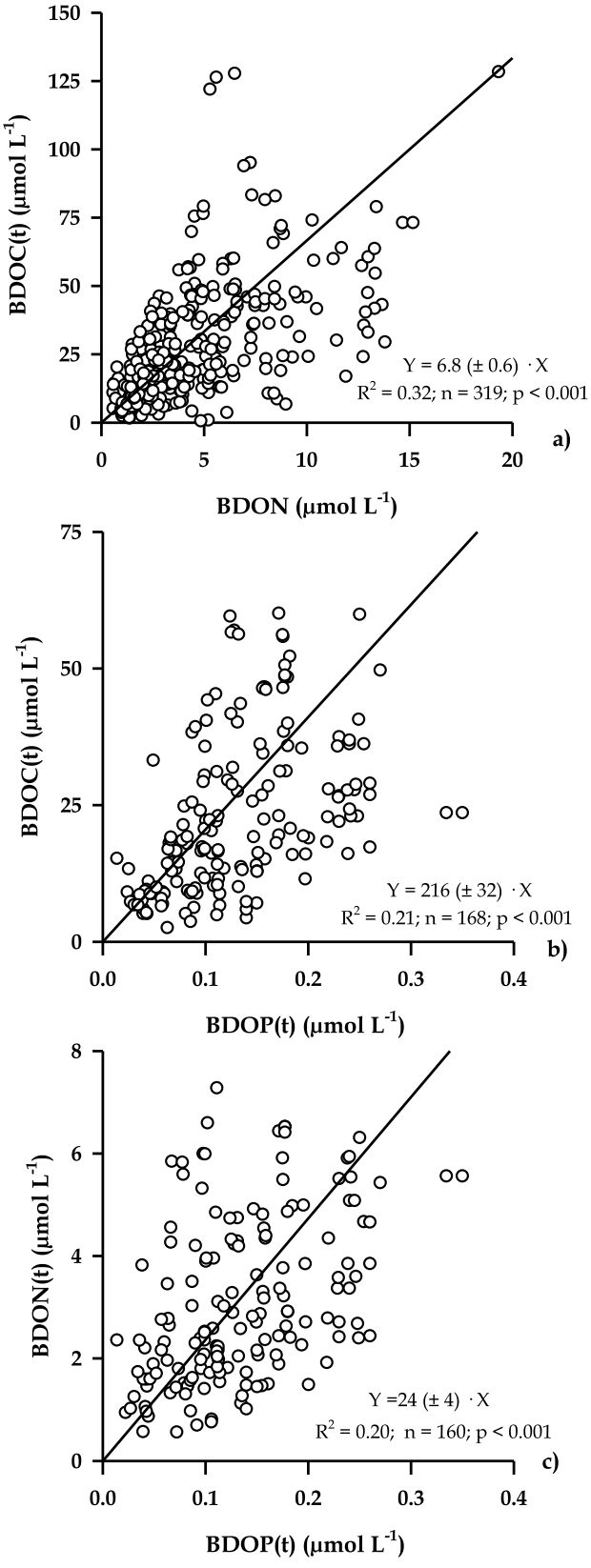

Figure 4. X-Y plots of the relationship between the concentrations of bioavailable (a) DOC and DON, (b) DOC and DOP, and (c) DON and DOP used at all incubation time in all experiments. Dashed line, 1:1 line; solid line, linear fitting equation according to *Sokal and Rohlf* [1995] model II.

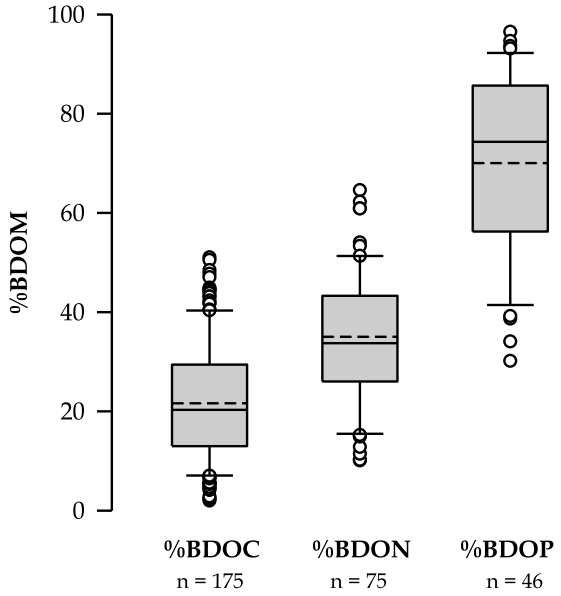

Figure 5. Box-and-whiskers plot of the proportions of DOC, DON, and DOP pools that are bioavailable in the coastal ocean, considering incubations experiments that lasted for >40 days. Fifty percent of the data are included within the limit of the boxes, and the caps represent the 10th and 90th percentiles. Solid lines represent the median and dotted line the mean value.

>40 days. The fraction of DOC utilized after the incubation time, BDOC, ranged from 1 to 199 μmol L^{-1}, representing from 2 to 51% of the total DOC pool, with a mean ± SD value of 22 ± 12% (n = 175). BDON concentrations varied between 0.6 to 15.2 μmol L^{-1}, representing between 10 and 65% of the DON pool, with a mean ± SD value of 35 ± 13% (n = 75). BDOP varied from 0.04 and 0.33 μmol L^{-1}, ranging from 30 to 96% of the total DOP pool with a mean ± SD value of 70 ± 18% (n = 45). A T-test of the mean ± SD values of the percentages of BDOM indicates that DOP is significantly ($p < 0.001$) more bioavailable than DON and the latter significantly ($p < 0.001$) more bioavailable than DOC (Figure 5).

[21] Regarding the pool that is resistant to microbial utilization after the incubation time, RDOM, its concentration can be estimated on basis of the initial salinity and DOM concentration of the incubated water sample, by means of the power function $RDOM = \alpha \cdot s^{\beta} \cdot DOM^{\gamma}$. The values of α, β and γ are summarized in Table 1. α is not significantly different from 1 in the three cases; therefore, the dependence of RDOM on DOM is linear for DOC, DON and DOP. β is negative and with an absolute value significantly lower than 1 for the cases of RDOC and RDON, indicating that the material of continental origin is more resistant than the material of marine origin. Conversely, RDOP does not vary significantly with salinity.

[22] Figure 6 shows the variability of the C: N: P stoichiometry of the bioavailable and resistant DOM pools. BDOM had a mean ± SD and median C: N molar ratios of 8.8 ± 4.4 (n = 69) and 7.5, respectively. By contrast, the resistant pool presented significantly higher ($p < 0.001$) mean ± SD and median values of 15.5 ± 4.6 (n = 69) and 14.2, respectively (Figure 6a). The same behavior was observed for the C: P molar ratio; the mean ± SD and median ratio for the BDOM pool were 25 ± 16 (n = 43) and 19, and for the RDOM pool they were 159 ± 187 (n = 43) and 73, respectively (Figure 6b). The C: N: P ratio of BDOM, 197 (±111): 25 (±16): 1 (mean ± SD) or 157: 19: 1 (median) was more N- and P- rich than the RDOM pool, 2835 (±3383): 159 (±187): 1 (mean ± SD) or 1191: 73: 1 (median).

[23] Figure 7 summarizes the variability of the first-order decay constants of BDOC, BDON and BDOP degradation referred to 15°C. BDOC presented mean ± SD and median values of κ_C of 0.066 ± 0.065 day^{-1} (n = 127) and 0.045 day^{-1}, respectively. The BDON degradation rate constants (κ_N) reached mean and median values of 0.111 ± 0.096 day^{-1} (n = 68) and 0.088 day^{-1}. For BDOP the degradation rate constants (κ_P) had mean and median values of 0.154 ± 0.137 day^{-1} (n = 42) and 0.106 day^{-1}, respectively. The first-order degradation rate constants of BDOM decreased significantly ($p < 0.05$) in the sequence $\kappa_P > \kappa_N > \kappa_C$. Power function relationships of the type $\kappa_X = \alpha + \beta \cdot \kappa_Y^{\gamma}$ existed among the three rate constants (Figure 8), with a high predicting power, $R^2 > 0.84$ (Table 1). A positive origin intercept $\alpha = 0.04 \pm 0.01$ day^{-1} occurs in the three relationships, suggesting a basal C degradation under N and/or P starvation. Parameters β and γ were significantly larger than 1 for the κ_C to κ_N relationship, 1.3 ± 0.2 and 1.7 ± 0.2, respectively. This means that although BDON is generally utilized faster than BDOC, this trend reverses at low (<0.04 day^{-1}) and high (>0.60 day^{-1}) κ_N values. Although the highest κ_N value recorded in the incubation experiments that lasted >40 days was <0.5 day^{-1}, in the case of the very short incubation experiments (3 days) in the coastal upwelling of Oregon, κ_N values of 0.71 day^{-1} were accompanied by higher values of κ_C of 0.95 day^{-1} (see Table S2). For the case of the relationship between κ_C and κ_P, β was significantly lower and γ significantly higher than 1; as a result, BDOP is mineralized faster than BDOC at any $\kappa_P > 0.04$ day^{-1}. An unrealistic

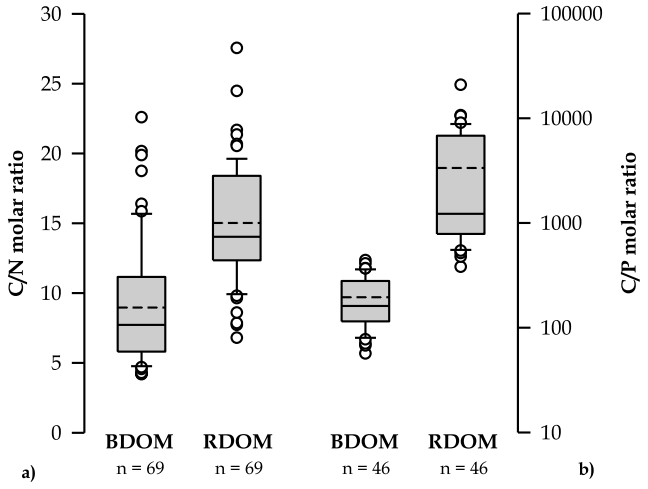

Figure 6. Box-and-whiskers plots of the (a) C: N and (b) N: P molar ratios of bioavailable and resistant DOM pools in the coastal ocean (incubations >40 days included). Fifty percent of the data are included within the limit of the boxes, and the caps represent the 10th and 90th percentiles. Solid lines represent the median and dotted line the mean value. Note the logarithmic scale of Figure 6b.

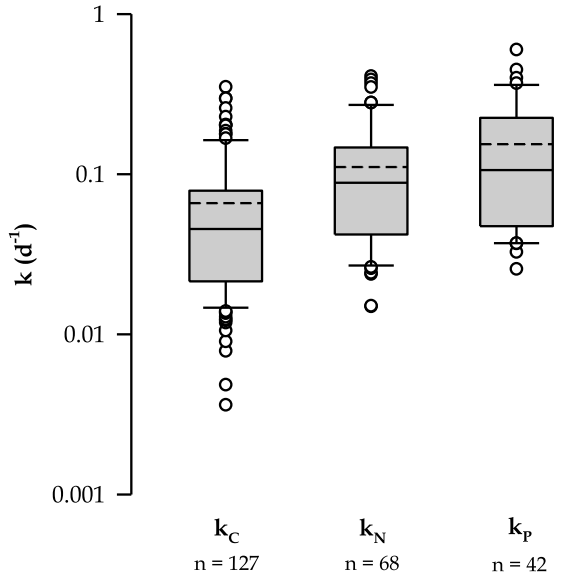

Figure 7. Box-and-whiskers plots of the first-order degradation rate constants (κ_C, κ_N, and κ_P) of BDOM calculated for incubation experiments lasting >40 days. Fifty percent of the data are included within the limit of the boxes, and the caps represent the 10th and 90th percentiles. Solid lines represent the median and dotted line the mean value. Note the logarithmic scale.

value of $\kappa_N > 2.22$ day^{-1} would be necessary to observe κ_C higher than κ_P. Finally, for the case of the relationship between κ_N and κ_P, γ is not significantly different from 1 and therefore, the relationship between the two rates is linear with a slope β of 0.8 $\pm$ 0.1.

4. Discussion

4.1. Bioavailability of DOM in the Coastal Ocean

[24] In all study sites, DOP was more bioavailable than DON and the latter more bioavailable than DOC (Table 1 and Figures 3 and 5). This sequence of bioavailability suggests that the role of the DOM pool on the recycled and export production of the coastal ocean is more relevant for the P than for the N, and for the N than for the C biogeochemical cycles [*Hopkinson and Vallino*, 2005; *Lønborg et al.*, 2010]. The observed variability of DOM bioavailability could be due to differences in incubation times, initial nutrient and temperature conditions, terrestrial inputs, UV-light exposure of the water samples prior to incubation or bacterial community and DOM chemical composition [*Del Giorgio and Davies*, 2003; *Kawasaki and Benner*, 2006; *Vähätalo and Jarvin*, 2007; *Lønborg et al.*, 2009a]. In this study we have shown that a simple power function of the incubation time and the initial DOM to salinity ratio, an index of the terrestrial/marine origin of the materials, is able to explain 31–57% of the variability of the degradation rate of BDOM(t). As the DOM in natural systems contains a complex mixture of organic compounds with changing lability, it is not surprising that the incubation time plays a major part in determining the BDOM amounts measured. Short term incubations (hours- days) will only include the most labile pools, while longer term incubations will measure both the labile and fractions of the semi-labile pool. The more refractory nature of the materials of terrestrial origin is confirmed by the significant negative relationship of RDOC and RDON with salinity (Table 1), suggesting that RDOM moved conservatively during its transition from the continent to the open ocean through the coastal zone.

[25] DOM availability has previously been shown to vary depending on the DOM chemical composition [*Benner and Opsahl*, 2001], contribution of allochthonous and autochthonous sources [*Lønborg and Søndergaard*, 2009], bacterial community composition [*Martinez et al.*, 1996], inorganic nutrient limitation [*Rivkin and Anderson*, 1997], protist grazing [*Thingstad et al.*, 1999], temperature [*Chen and Wangersky*, 1996], production of refractory components [*Lønborg et al.*, 2009b], protection of compounds by submicron particles [*Stoderegger and Herndl*, 1998], as well as photochemical processes [*Kieber et al.*, 1997]. In this study we only have in situ nutrient and temperature measurements: No significant relationships were found between BDOM and these parameters, suggesting that they were not major players in determining the DOM bioavailability when all data are gatherer together (data not shown). Given that the incubation experiments analyzed in this work were conducted in the dark, the influence of natural UV radiation on the bioavailability and utilization rate of DOM during the incubation time cannot be assessed. Although contrasting results have been reported in the literature on the effect of UV-light of DOM bioavailability, the currently accepted consensus is that the refractory material of either terrestrial or marine origin gets more bioavailable after exposure to natural light, whereas the freshly produced organic biomolecules become more resistant after exposure [*Kieber et al.*, 1997; *Obernosterer et al.*, 1999; *Megali Amado et al.*, 2007].

4.2. Stoichiometry of the Bioavailable and Resistant DOM in the Coastal Ocean

[26] Our C: N: P ratios of BDOM for the coastal ocean (Figures 4 and 6) are compatible with those previously reported by *Benner* [2002], 300: 22:1, and by *Hopkinson and Vallino* [2005], 199: 20: 1 for the open ocean. These ratios, 216 ($\pm$32): 24 ($\pm$4): 1 from the continuum reaction model or 197 ($\pm$111): 25 ($\pm$16): 1 from the multi-G model, are not significantly different among them. They are quite close to the average C: N: P stoichiometry of marine phytoplankton (106: 16: 1) [*Redfield et al.*, 1963] and phytoplankton produced DOM (170: 6.5: 1) [*Conan et al.*, 2007], strongly suggesting the planktonic origin of BDOM in the coastal ocean. The higher C: P and N: P of BDOM compared with the Redfield ratio could either be due to plankton release of C-rich labile compounds such as mono- and polysaccharides under in situ nutrient-depleted conditions [*Fajon et al.*, 1999] and/or the selective degradation of N- and/or P-rich compounds [*Hopkinson et al.*, 1997].

[27] The C: N: P ratio of RDOM, 2835 ($\pm$3383): 159 ($\pm$187): 1, was extremely N- and P- depleted compared with the BDOM pool but it was compatible with the C: N: P ratio reported by *Hopkinson and Vallino* [2005] for refractory marine DOM, 3511: 202: 1, and comparable to the C: N: P ratio of terrestrial refractory DOM, 3495: 118: 1, reported by *Meybeck* [1982]. Comparatively, DOC and DON concentrations in the surface layer of mid-ocean gyres range

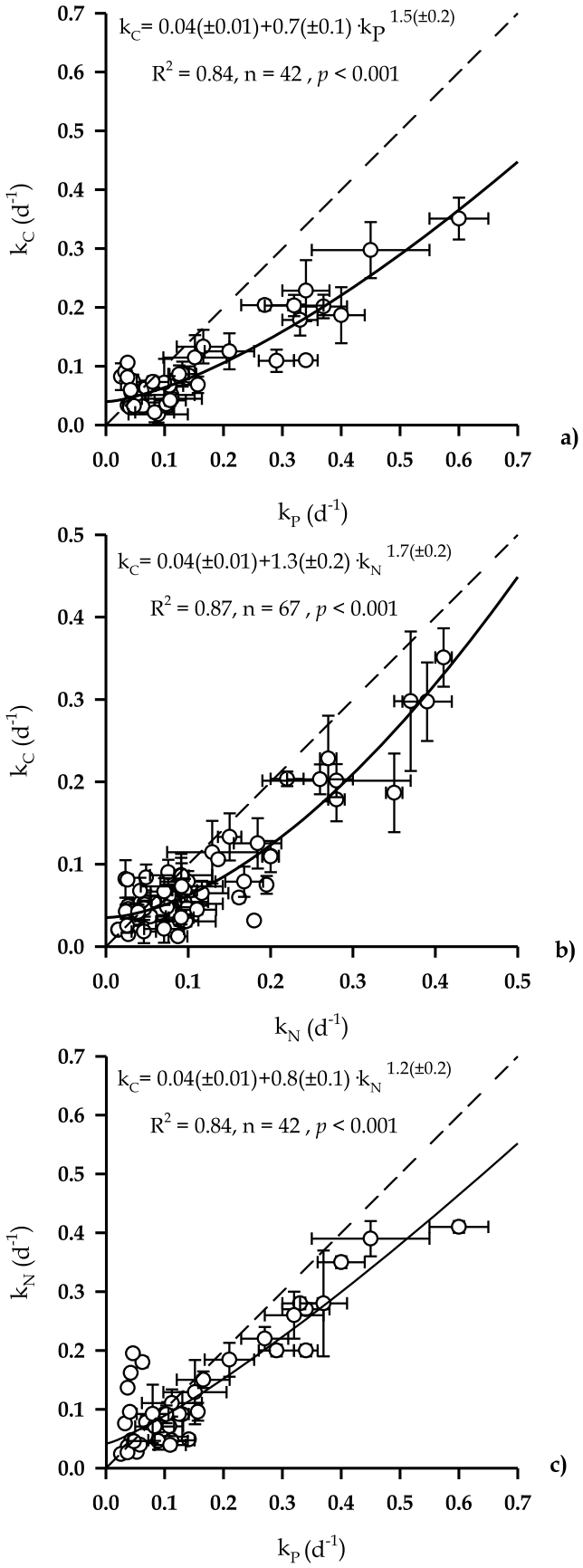

Figure 8. X-Y plots of (a) κ_C versus κ_N, (b) κ_C versus κ_P, and (c) κ_N versus κ_P for incubation experiments lasting for >40 days. Fifty percent of the data are included within the limit of the boxes, and the caps represent the 10th and 90th percentiles. Dashed line, 1:1 line; solid line, power fitting equation using the Marquardt-Levenberg algorithm implemented in the software package Statistica 6.0. See fitting parameters in Table 1.

from 65–80 and 5–6 μmol L^{-1} [*Hansell et al.*, 2009] respectively, which produce a C: N molar ratio of 13 ± 4, not significantly different from our C: N ratio of RDOM of 15 ± 4. C: P ratios in the surface open ocean are very variable depending on the relative importance of N_2 fixation that, in turns, is conditioned by iron availability [*Mather et al.*, 2008].

4.3. DOM Utilization Rates in the Coastal Ocean

[28] Significant power relations were found between κ_C, κ_N and κ_P, (Table 1) with fitting parameters indicating that BDOP is utilized faster than BDON and the latter faster than BDOC except at κ_N and κ_P values <0.04 day^{-1} and κ_N values >0.60 day^{-1}. This fractionation during the utilization of DOM is consistent with our C: N: P stoichiometry data and as well as with previous studies investigating organic matter utilization in marine waters [*Garber*, 1984; *Hopkinson et al.*, 1997]. It should be noticed that the utilization rate constants were normalized to 15°C using Q_{10} values of 2.2, 2.0 and 1.5 for C, N and P compounds, respectively. According to the Arrhenius theory, a lower value of Q_{10} indicates lower activation energy of the enzymatic reactions, which can be interpreted also as indicative of a higher bioavailability of the substrate, as recently suggested for the microbial degradation of organic matter in soils [*Davidson and Janssens*, 2006]. With these considerations in mind, the sequence of Q_{10} values are consistent with the sequence of P > N > C lability.

[29] The fate, utilization versus export, as well as the stoichiometry and bioavailability of the material exported from the coastal to the open ocean will depend on the balance between the half-life time of the BDOM pool, ln2/κ_M, and the flushing time of water in the coastal ocean, $\tau = V/Q_E$, where V is the volume and Q_E the water exchanged with the adjacent continent and open ocean. Considering the mean values of the degradation rate constants obtained in this work (Figure 7), half-life times of 10.5, 6.2 and 4.5 day are obtained for BDOC, BDON and BDOP, respectively. Comparatively, τ ranges from a few days in very dynamic systems such as coastal upwelling areas to several months in arid enclosed bays [*Brink*, 1998; *Laurelle et al.*, 2009]. For reference, the half-life time of the semi-labile, semi-refractory and refractory DOC that occupies the dark ocean is 1.5, 20 and 16000 years [*Hansell et al.*, 2012] and the flushing time of water ranges from about 80 years for the intermediate and 2000 years for deep ocean [*Laurelle et al.*, 2009].

[30] When the flushing time coincides with the half life time of BDOC, 50% of the BDOC, 67% of the BDON and 80% of the BDOP will be processed in the coastal ocean and the remaining fractions will be exported to the adjacent ocean, where it could contribute to feed the microbial populations living there. Figure 9 shows the evolution of the C: N and C: P stoichiometry of BDOM as a function of its

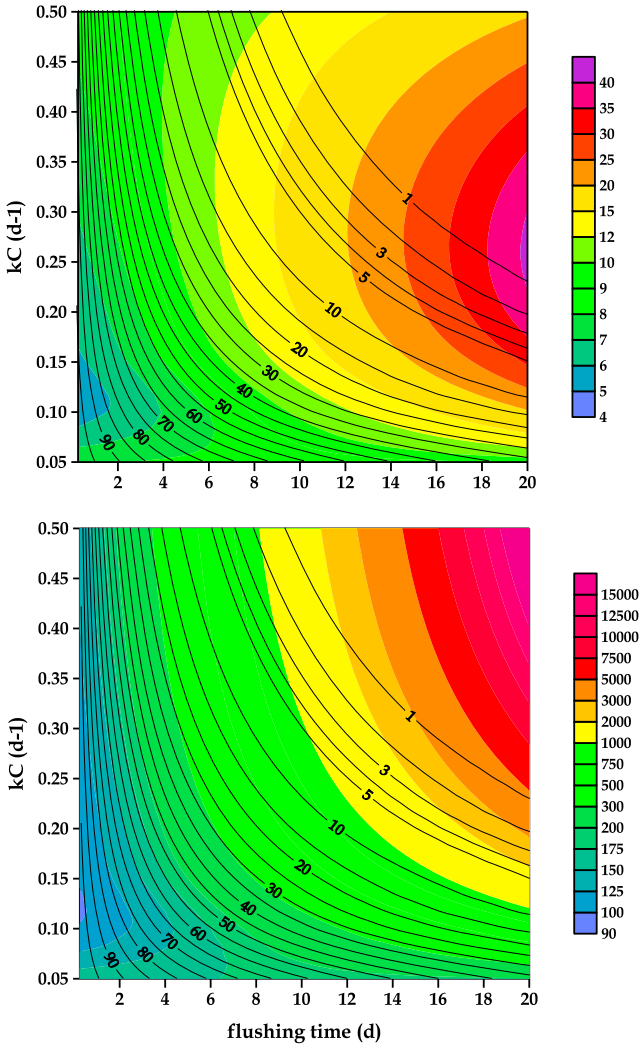

Figure 9. (top) C: N and (bottom) C: P molar ratio of the BDOM used in the coastal ocean as a function of the degradation rate and the flushing time. The superimposed solid lines correspond to the percentage of the initial bioavailable DOC that has not been utilized.

lability, expressed as κ_C, and the flushing time. The values of κ_N, and κ_P, needed to calculate the stoichiometry, were obtained from the relationships with κ_C, presented in Table 1. Note that, as a consequence of the power relationship between the utilization rate constants (Figure 8 and Table 1) the isolines of the C: N: P stoichiometry of BDOM utilization (color background) were not parallel to the isolines of the percentage of unused BDOC (solid black lines) (Figure 9). Initially, the substrates are utilized at very low C: N molar ratios, close to 4, which would be compatible with the preferential utilization of amino acids and/or nucleotides with average biochemical composition of $C_{138}H_{127}O_{45}N_{39}S$ and $C_{45}H_{76}O_{31}N_{12}P_5$ respectively in marine phytoplankton [*Anderson*, 1995; *Fraga et al.*, 1998]. The C: N utilization molar ratio increases up to 40 after an incubation period of 20 days at a rate of 0.15 day^{-1}. A similar trend is observed for the C: P utilization molar ratio, which increases from about 90 to more than 1000 after 20 days decomposing at a rate of 0.15 day^{-1}. Therefore, the coastal BDOM exported horizontally is carbon rich and, consequently, its utilization in the adjacent ocean could depend on the supply of inorganic N and P [e.g., *Thingstad et al.*, 1997].

5. Conclusions

[31] Our meta-analysis suggests that coastal plankton communities and terrestrial inputs control the concentration and stoichiometry of the bioavailable and resistant fractions of coastal DOM, respectively. At least 4% of the global net primary production (NPP) of the coastal zone is exported to the adjacent open ocean as DOM [*Chen*, 2003]. This proportion rises to more than 20% in coastal upwelling filaments [*Álvarez-Salgado et al.*, 2007]. Assuming a NPP of 6.5 Pg C year^{-1} [*Dunne et al.*, 2007] for the global coastal ocean, about 0.3 Pg C year^{-1} are exported as DOC to the open ocean, a number that represents about 15% of global marine primary production that accumulate each year as DOC [*Hansell et al.*, 2009]. The ratio between the half-life time of BDOM and the flushing time of any particular coastal system will dictate the fate (in situ degradation *versus* export) and the quality (C: N: P ratio) of the coastal BDOM that, in turns, conditions the fate of the exported BDOM in the adjacent ocean (degradation *versus* accumulation). Inorganic N and/or P limitation in stratified adjacent ocean surface waters would provoke the accumulation of an extremely N- and P-poor exported BDOM up to the time of winter mixing [*Carlson et al.*, 1994]. Our data, in conjugation with other recent studies [*Mather et al.*, 2008; *Torres-Valdés et al.*, 2009] support the hypothesis that large scale export of BDOM is fuelling parts of the oceanic new production and influence the N/P limitation of the open ocean.

[32] **Acknowledgments.** This study was funded by a Marie Curie fellowship from the Early stage Training site ECOSUMMER (MEST-CT-2004-020501) and a grant from the Carlsberg Foundation to C.L. X.A.A.-S. has been partially funded by projects IMAN (07MMA002402PR) and CAIBEX (CTM2007-66408-C02-01/MAR). The results supplied by Morten Søndergaard, Risto Lignell, Peter A. Raymond, Takehiko Fukushima, Toru Hasegawa, Yasuaki Tanaka, and William V. Sobczak are highly appreciated.

References

Álvarez-Salgado, X. A., J. Arístegui, E. D. Barton, and D. A. Hansell (2007), Contribution of upwelling filaments to offshore carbon export in the subtropical northeast Atlantic Ocean, *Limnol. Oceanogr.*, *52*, 1287–1292, doi:10.4319/lo.2007.52.3.1287.

Amon, R. M. W., and R. Benner (1996), Bacterial utilization of different size classes of dissolved organic matter, *Limnol. Oceanogr.*, *41*, 41–51, doi:10.4319/lo.1996.41.1.0041.

Anderson, L. A. (1995), On the hydrogen and oxygen content of marine phytoplankton, *Deep Sea Res., Part I*, *42*, 1675–1680, doi:10.1016/0967-0637(95)00072-E.

Badr, E.-S. A., A. D. Tappin, and E. P. Achterberg (2008), Distributions and seasonal variability of dissolved organic nitrogen in two estuaries in SW England, *Mar. Chem.*, *110*, 153–164, doi:10.1016/j.marchem.2008.04.007.

Bauer, J. E., P. M. Williams, and E. R. M. Druffel (1992), ^{14}C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea, *Nature*, *357*, 667–670, doi:10.1038/357667a0.

Beaupré, S. R., and E. R. M. Druffel (2009), Constraining the propagation of bomb-radiocarbon through the dissolved organic carbon (DOC) pool in the northeast Pacific Ocean, *Deep Sea Res., Part I*, *56*, 1717–1726, doi:10.1016/j.dsr.2009.05.008.

Bekins, B. A., E. Warren, and E. M. Godsy (1998), A comparison of zero-order, first-order, and monod biotransformation models, *Ground Water*, *36*, 261–268, doi:10.1111/j.1745-6584.1998.tb01091.x.

Benner, R. (2002), Chemical composition and reactivity, in *Biogeochemistry of Marine Dissolved Organic Matter*, edited by D. A. Hansell and C. A.

Carlson, pp. 59–90, Academic, San Diego, Calif., doi:10.1016/B978-012323841-2/50005-1.

Benner, R., and S. Opsahl (2001), Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume, *Org. Geochem.*, *32*, 597–611, doi:10.1016/S0146-6380(00)00197-2.

Brink, K. H. (1998), Deep-sea forcing and exchange processes, in *The Sea*, vol. 10, *The Global Coastal Ocean: Processes and Methods*, edited by K. H. Brink and A. R. Robinson, pp. 151–168, John Wiley, New York.

Bronk, D. A., and P. M. Glibert (1993), Application of a ^{15}N tracer method to the study of dissolved organic nitrogen uptake during spring and summer in Chesapeake Bay, *Mar. Biol. Berlin*, *115*, 501–508, doi:10.1007/BF00349849.

Burdige, D. J., S. W. Kline, and W. Chen (2004), Fluorescent dissolved organic matter in marine sediment pore waters, *Mar. Chem.*, *89*, 289–311, doi:10.1016/j.marchem.2004.02.015.

Carlson, C. A. (2002), Chemical composition and reactivity, in *Biogeochemistry of Marine Dissolved Organic Matter*, edited by D. A. Hansell and C. A. Carlson, pp. 91–151, Academic, San Diego, Calif., doi:10.1016/B978-012323841-2/50006-3.

Carlson, D. J., L. M. Mayer, M. L. Brann, and T. H. Mague (1985), Binding of monomeric organic compounds to macromolecular dissolved organic matter in seawater, *Mar. Chem.*, *16*, 141–153, doi:10.1016/0304-4203(85)90019-2.

Carlson, C. A., H. W. Ducklow, and A. F. Michaels (1994), Annual flux of dissolved organic carbon from the euphotic zone in the north-western Sargasso Sea, *Nature*, *371*, 405–408, doi:10.1038/371405a0.

Cauwet, G. (2002), DOM in coastal areas, in *Biogeochemistry of Marine Dissolved Organic Matter*, edited by D. A. Hansell and C. A. Carlson, pp. 579–609, Academic, San Diego, Calif., doi:10.1016/B978-012323841-2/50014-2.

Chen, C. T. A. (2003), New vs. export production on the continental shelf, *Deep Sea Res., Part II*, *50*, 1327–1333, doi:10.1016/S0967-0645(03)00026-2.

Chen, W., and P. J. Wangersky (1996), Rates of microbial degradation of dissolved organic carbon from phytoplankton cultures, *J. Plankton Res.*, *18*, 1521–1533, doi:10.1093/plankt/18.9.1521.

Chin, W. C., M. V. Orellana, and P. Verdugo (1998), Spontaneous assembly of marine dissolved organic matter into polymer gels, *Nature*, *391*, 568–572.

Chróst, R. J., and H. Rai (1993), Ectoenzyme activity and bacterial secondary production in nutrient impoverished and nutrient-enriched freshwater mesocosms, *Microb. Ecol.*, *25*, 131–150, doi:10.1007/BF00177191.

Coffin, R. B., J. P. Connolly, and P. S. Harris (1993), Availability of dissolved organic carbon to bacterioplankton examined by oxygen utilization, *Mar. Ecol. Prog. Ser.*, *101*, 9–22, doi:10.3354/meps101009.

Conan, P., et al. (2007), Partitioning of organic production in marine plankton communities: The effects of inorganic nutrient ratios and community composition on new dissolved organic matter, *Limnol. Oceanogr.*, *52*, 753–765, doi:10.4319/lo.2007.52.2.0753.

Cornell, S. E., A. R. Rendell, and T. D. Jickells (1995), Atmospheric deposition of organic nitrogen, *Nature*, *376*, 243–246, doi:10.1038/376243a0.

Davidson, E. A., and I. Janssens (2006), Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, *Nature*, *440*, 165–173, doi:10.1038/nature04514.

Del Giorgio, P. A., and J. Davies (2003), Patterns of dissolved organic matter lability and consumption across aquatic ecosystems, in *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, edited by S. E. G. Findlay and R. L. Sinsabaugh, pp. 399–424, Academic, San Diego, Calif.

Dundas, I. E. D. (1985), Fate and possible effects of excessive sperm released during spawning, *Mar. Ecol. Prog. Ser.*, *30*, 287–290, doi:10.3354/meps030287.

Dunne, J. P., J. L. Sarmiento, and A. Gnanadesikan (2007), A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on seafloor, *Global Biogeochem. Cycles*, *21*, GB4006, doi:10.1029/2006GB002907.

Fajon, C., G. Cauwet, P. Lebaron, S. Terzic, M. Ahel, A. Malej, P. Mozetic, and V. Turk (1999), The accumulation and release of polysaccharides in plankton cells and the subsequent bacterial response during a controlled experiment, *FEMS Microbiol. Ecol.*, *29*, 351–363, doi:10.1111/j.1574-6941.1999.tb00626.x.

Fraga, F., A. F. Ríos, F. F. Pérez, and F. G. Figueiras (1998), Theoretical limits of oxygen: Carbon and oxygen:nitrogen ratios during photosynthesis and mineralization of organic matter in the sea, *Sci. Mar.*, *62*, 161–168, doi:10.3989/scimar.1998.62n1-2161.

Garber, J. H. (1984), Laboratory study of nitrogen and phosphorus remineralization during the decomposition of coastal plankton and seston, *Estuarine Coastal Shelf Sci.*, *18*, 685–702, doi:10.1016/0272-7714(84)90039-8.

Gattuso, J.-P., M. Frankignoulle, and R. Wollast (1998), Carbon and carbonate metabolism in coastal aquatic ecosystems, *Annu. Rev. Ecol. Syst.*, *29*, 405–434, doi:10.1146/annurev.ecolsys.29.1.405.

Hansell, D. A., C. A. Carlson, D. J. Repeta, and R. Schlitzer (2009), Dissolved organic matter in the ocean: New insights stimulated by a controversy, *Oceanography*, *22*, 202–211, doi:10.5670/oceanog.2009.109.

Hansell, D. A., C. A. Carlson, and R. Schlitzer (2012), Net removal of major marine dissolved organic carbon fractions in the subsurface ocean, *Global Biogeochem. Cycles*, *26*, GB1016, doi:10.1029/2011GB004069.

Hill, J. K., and P. A. Wheeler (2002), Organic carbon and nitrogen in the northern California current system: Comparison of offshore, river plume, and coastally upwelled water, *Prog. Oceanogr.*, *53*, 369–387, doi:10.1016/S0079-6611(02)00037-X.

Hopkinson, C. S., and J. J. Vallino (2005), Efficient export of carbon to the deep ocean through dissolved organic matter, *Nature*, *433*, 142–145, doi:10.1038/nature03191.

Hopkinson, C. S., B. Fry, and A. L. Nolin (1997), Stoichiometry of dissolved organic matter dynamics on the continental shelf of the northeastern U.S, *Cont. Shelf Res.*, *17*, 473–489, doi:10.1016/S0278-4343(96)00046-5.

Kawasaki, N., and R. Benner (2006), Bacterial release of dissolved organic matter during cell growth and decline: Molecular origin and composition, *Limnol. Oceanogr.*, *51*, 2170–2180, doi:10.4319/lo.2006.51.5.2170.

Kieber, R. J., L. H. Hydro, and P. J. Seaton (1997), Photooxidation of triglycerides and fatty acids in seawater: Implication toward the formation of marine humic substances, *Limnol. Oceanogr.*, *42*, 1454–1462, doi:10.4319/lo.1997.42.6.1454.

Kirchman, D. L. (2000), Uptake and regeneration of inorganic nutrients by marine heterotrophic bacteria, in *Microbial Ecology of the Oceans*, edited by D. L. Kirchman, pp. 261–288, John Wiley, Hoboken, N. J.

Laurelle, G. G., et al. (2009), Anthropogenic perturbations of the silicon cycle at the global scale: Key role of the land-ocean transition, *Global Biogeochem. Cycles*, *23*, GB4031, doi:10.1029/2008GB003267.

Lønborg, C., and M. Søndergaard (2009), Microbial availability and degradation of dissolved organic carbon and nitrogen in two coastal areas, *Estuarine Coastal Shelf Sci.*, *81*, 513–520.

Lønborg, C., K. Davidson, X. A. Álvarez–Salgado, and A. E. J. Miller (2009a), Bioavailability and bacterial degradation rates of dissolved organic matter in a temperate coastal area during an annual cycle, *Mar. Chem.*, *113*, 219–226, doi:10.1016/j.marchem.2009.02.003.

Lønborg, C., X. A. Álvarez-Salgado, K. Davidson, and A. E. J. Miller (2009b), Production of bioavailable and refractory dissolved organic matter by coastal heterotrophic microbial populations, *Estuarine Coastal Shelf Sci.*, *82*, 682–688, doi:10.1016/j.ecss.2009.02.026.

Lønborg, C., X. A. Álvarez–Salgado, S. Garcia-Martinéz, A. E. J. Miller, and E. Teira (2010), Stoichiometry of dissolved organic matter and the kinetics of its microbial degradation in a coastal upwelling system, *Aquat. Microb. Ecol.*, *58*, 117–126, doi:10.3354/ame01364.

Martinez, J., D. C. Smith, G. F. Steward, and F. Azam (1996), Variability in ectohydrolytic enzyme activities of pelagic marine bacteria and its significance for substrate processing in the sea, *Aquat. Microb. Ecol.*, *10*, 223–230, doi:10.3354/ame010223.

Mather, R. L., S. E. Reynolds, G. A. Wolff, R. G. Williams, S. Torres-Valdes, X. Pan, E. M. S. Woodward, R. Sanders, and E. P. Achterberg (2008), Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres, *Nat. Geosci.*, *1*, 439–443, doi:10.1038/ngeo232.

Megali Amado, A., J. B. Cotner, A. L. Suhett, F. A. Esteves, R. L. Bozelli, and V. F. Farjalla (2007), Contrasting interactions mediate dissolved organic matter decomposition in tropical aquatic ecosystems, *Aquat. Microb. Ecol.*, *49*, 25–34, doi:10.3354/ame01131.

Meybeck, M. (1982), Carbon, nitrogen and phosphorus transport by world rivers, *Am. J. Sci.*, *282*, 401–450, doi:10.2475/ajs.282.4.401.

Middelburg, J. J., T. Vlug, and F. J. W. A. van der Nat (1993), Organic matter mineralization in marine systems, *Global Planet. Change*, *8*, 47–58, doi:10.1016/0921-8181(93)90062-S.

Monod, J. (1949), The growth of bacterial cultures, *Annu. Rev. Microbiol.*, *3*, 371–394, doi:10.1146/annurev.mi.03.100149.002103.

Moran, M. A., and R. G. Zepp (1997), Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter, *Limnol. Oceanogr.*, *42*, 1307–1316, doi:10.4319/lo.1997.42.6.1307.

Mou, X., R. E. Hodson, and M. A. Moran (2007), Bacterioplankton assemblages transforming dissolved organic compounds in coastal seawater, *Environ. Microbiol.*, *9*, 2025–2037, doi:10.1111/j.1462-2920.2007.01318.x.

Mou, X., S. Sun, R. A. Edwards, R. E. Hodson, and M. A. Moran (2008), Bacterial carbon processing by generalist species in the coastal ocean, *Nature*, *451*, 708–711, doi:10.1038/nature06513.

Nedwell, D. B. (1999), Effect of low temperature on microbial growth: Lowered affinity for substrates limits growth at low temperature, *FEMS Microbiol. Ecol.*, *30*, 101–111.

Obernosterer, I., B. Reitner, and G. J. Herndl (1999), Contrasting effects of solar radiation on dissolved organic matter and its bioavailability to marine bacterioplankton, *Limnol. Oceanogr.*, *44*, 1645–1654, doi:10.4319/lo.1999.44.7.1645.

Ogura, N. (1972), Rate and extent of decomposition of dissolved organic matter in surface seawater, *Mar. Biol. Berlin*, *13*, 89–93, doi:10.1007/BF00366559.

Ogura, N. (1975), Further studies on decomposition of dissolved organic matter in coastal waters, *Mar. Biol. Berlin*, *31*, 101–111, doi:10.1007/BF00391622.

Pempkowiak, J. (1985), The input of biochemically labile and resistant organic matter to the Baltic Sea from the Vistula River, *Mitt. Geol. Palaeontol. Inst. Univ. Hamburg*, *85*, 345–350.

Pomeroy, L. R. (1974), The oceans food web, a changing paradigm, *BioScience*, *24*, 499–504, doi:10.2307/1296885.

Raymond, P. A., and J. E. Bauer (2000), Bacterial consumption of DOC during transport through a temperate estuary, *Aquat. Microb. Ecol.*, *22*, 1–12, doi:10.3354/ame022001.

Redfield, A. C., B. K. Ketchum, and F. A. Richards (1963), The influence of organisms on the composition of sea-water, in *The Sea*, vol. 2, *The Composition of Sea Water: Comparative and Descriptive Oceanography*, edited by M. N. Hill, pp. 26–77, Wiley-Interscience, Hoboken, N. J.

Rivkin, R. B., and M. R. Anderson (1997), Inorganic nutrient limitation of oceanic bacterioplankton, *Limnol. Oceanogr.*, *42*, 730–740, doi:10.4319/lo.1997.42.4.0730.

Seiki, T., E. Date, and H. Izawa (1991), Decomposition characteristics of particulate organic matter in Hiroshima Bay, *J. Oceanogr.*, *47*, 207–220.

Sholkovitz, E. R. (1976), Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, *Geochim. Cosmochim. Acta*, *40*, 831–845, doi:10.1016/0016-7037(76)90035-1.

Smith, S. V., and J. T. Hollibaugh (1997), Annual cycle and interannual variability of ecosystem metabolism in a temperate climate embayment, *Ecol. Monogr.*, *67*, 509–533, doi:10.1890/0012-9615(1997)067[0509:ACAIVO]2.0.CO;2.

Smith, D. C., M. Simon, A. L. Alldredge, and F. Azam (1992), Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution, *Nature*, *359*, 139–142, doi:10.1038/359139a0.

Sobczak, W. V., J. E. Cloern, A. D. Jassby, B. E. Cole, T. S. Schraga, and A. Arnberg (2005), Detritus fuels ecosystem metabolism but not metazoan food webs in San Francisco estuary's freshwater delta, *Estuaries Coasts*, *28*, 124–137, doi:10.1007/BF02732759.

Sokal, F. F., and F. J. Rohlf (1995), *Biometry: The Principles and Practice of Statistics in Biological Research*, 3rd ed., 887 pp., W. H. Freeman, New York.

Søndergaard, M. (1981), Kinetics of extracellular release of ^{14}C-labelled organic carbon by submerged macrophytes, *Oikos*, *36*, 331–347, doi:10.2307/3544631.

Søndergaard, M., and M. Middelboe (1995), A cross-systems analysis of labile dissolved organic carbon, *Mar. Ecol. Prog. Ser.*, *118*, 283–294, doi:10.3354/meps118283.

Søndergaard, M., P. J. B. Williams, G. Cauwet, B. Riemann, C. Robinson, S. Terzic, E. M. S. Woodward, and J. Worm (2000), Net accumulation and flux of dissolved organic carbon and dissolved organic nitrogen in marine plankton communities, *Limnol. Oceanogr.*, *45*, 1097–1111, doi:10.4319/lo.2000.45.5.1097.

Stoderegger, K., and G. J. Herndl (1998), Production and release of bacterial capsular material and its subsequent utilization by marine bacterioplankton, *Limnol. Oceanogr.*, *43*, 877–884, doi:10.4319/lo.1998.43.5.0877.

Thingstad, T. F., Å. Hagstrom, and F. Rassoulzadegan (1997), Accumulation of degradable DOC in surface waters: Is it caused by a malfunctioning microbial loop?, *Limnol. Oceanogr.*, *42*, 398–404, doi:10.4319/lo.1997.42.2.0398.

Thingstad, T. F., H. Havskum, H. Kaas, T. G. Nielsen, B. Riemann, D. Lefevre, and P. J. B. Williams (1999), Bacteria-protist interactions and organic matter degradation under P-limited conditions: Analysis of an enclosure experiment using a simple model, *Limnol. Oceanogr.*, *44*, 62–79, doi:10.4319/lo.1999.44.1.0062.

Torres-Valdés, S., V. M. Roussenov, R. Sanders, S. Reynolds, X. Pan, R. Mather, A. Landolfi, G. A. Wolff, E. P. Achterberg, and R. G. Williams (2009), Distribution of dissolved organic nutrients and their effect on export production over the Atlantic Ocean, *Global Biogeochem. Cycles*, *23*, GB4019, doi:10.1029/2008GB003389.

Vähätalo, A. V., and M. Jarvin (2007), Photochemically produced bioavailable nitrogen from biologically recalcitrant dissolved organic matter stimulates production of a nitrogen limited microbial food web in the Baltic Sea, *Limnol. Oceanogr.*, *52*, 132–143, doi:10.4319/lo.2007.52.1.0132.

Veuger, B., J. J. Middelburg, H. T. S. Boschker, J. Nieuwenhuize, P. V. Rijswijk, E. J. Rochelle-Newall, and N. Navarro (2004), Microbial uptake of dissolved organic and inorganic nitrogen in Randers Fjord, *Estuarine Coastal Shelf Sci.*, *61*, 507–515, doi:10.1016/j.ecss.2004.06.014.

Wada, S., M. N. Aoki, A. Mikami, T. Komatsu, Y. Tsuchiya, T. Sato, H. Shinagawa, and T. Hama (2008), Bioavailability of macroalgal dissolved organic matter in seawater, *Mar. Ecol. Prog. Ser.*, *370*, 33–44, doi:10.3354/meps07645.

Waksman, S. A., and C. L. Carey (1935), Decomposition of organic matter in sea water by bacteria: I. Bacterial multiplication in stored sea water, *J. Bacteriol.*, *29*, 531–543.

Walsh, J. J. (1991), Importance of continental margins in the marine biochemical cycling of carbon and nitrogen, *Nature*, *350*, 53–55, doi:10.1038/350053a0.

Williams, P. J. B. (1981), Incorporation of microheterotrophic processes into the classical paradigm of planktonic food web, *Kiel. Meeresforsch. Sonderh.*, *5*, 1–28.

Williams, P. J. B. (1995), Evidence for the seasonal accumulation of carbon-rich dissolved organic material, its scale in comparison with changes in particulate material and the consequential effect on net C/N assimilation ratios, *Mar. Chem.*, *51*, 17–29, doi:10.1016/0304-4203(95)00046-T.

Williams, P. M., and E. R. M. Druffel (1987), Radiocarbon in dissolved organic matter in the central North Pacific Ocean, *Nature*, *330*, 246–248, doi:10.1038/330246a0.

Wollast, R. (1998), Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, in *The Sea*, vol. 10, *The Global Coastal Ocean: Processes and Methods*, edited by K. H. Brink and A. R. Robinson, pp. 213–252, John Wiley, Hoboken, N. J.

Zweifel, U. L., B. Norrman, and Å. Hagstrom (1993), Consumption of dissolved organic carbon by marine bacteria and demand for inorganic nutrients, *Mar. Ecol. Prog. Ser.*, *101*, 23–32, doi:10.3354/meps101023.

Zweifel, U. L., J. Wikner, Å. Hagström, E. Lundberg, and B. Norrman (1995), Dynamics of dissolved organic carbon in a coastal ecosystem, *Limnol. Oceanogr.*, *40*, 299–305, doi:10.4319/lo.1995.40.2.0299.